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Surface Functionalization of Micro Mechanical Cantilever Sensors by Organic Capped TiO_2 and Fe_2O_3 Nanocrystals

C. Ingrosso[1,2]*, M. Striccoli[2], A. Agostiano[1,2], E. Sardella[3], S. Keller[4], G. Blagoi[4], A. Boisen[4], M. L. Curri[2]

[1]*Dep. di Chimica, Università di Bari, via Orabona 4, Bari 70126, Italy*
[2]*CNR-IPCF Sez. Bari c/o Dip. di Chimica, Università di Bari, via Orabona 4, Bari 70126, Italy*
[3]*CNR Institute of Inorganic Methods and Plasmas (IMIP), via Orabona 4, Bari 70126, Italy*
[4]*Dep. of Micro and Nanotechnology (MIC), Technical University of Denmark (DTU), Build. 345 East, Kgs. Lyngby 2800, Denmark*

Abstract

A convenient and rapid procedure has been achieved to immobilize densely packed nanoporous 3D arrays of oleic acid (OLEA)-capped rod-shaped TiO_2 nanocrystals (NCs) and nearly spherical Fe_2O_3 NCs on the surface of micro mechanical cantilever sensors on SU-8. The NCs have been immobilized at room temperature and in the dark on the micro cantilevers before their release. AFM, SEM and XPS investigations attest for an effective and attachment of the NCs on the SU-8 which occurs with not modifying the original morphology and chemical composition of the nano-objects allowing for an effective accomplishment of the cantilever fabrication.

Keywords: colloidal nanocrystals; SU-8; micro mechanical cantilever sensors; immobilization

1. Introduction

Micrometer-sized cantilevers represent an innovative class of ultrasensitive microelectro-mechanical system (MEMS) based sensors. Such microcomponents can be considered a universal sensor platform for measuring a multitude of physical and bio/chemical phenomena in different chemical environments, according to the proprieties of the cantilever coating. When a process such as a molecular adsorption occurs on a single side of the microcantilever, this one bends because of a change in surface stress which is sensitively detected by using different techniques[1]. Recently, the sensitivity of such sensors has been improved thanks to the employment of a new structural polymer, namely SU-8 characterized by a low Young's modulus[1]. The surface of SU-8 possesses free epoxy groups, which provide good accessibility to reactive bio/molecules with a high immobilization capability in controlled operating conditions[2], as well. Such a reactivity combined with the biocompatibility of the polymer has been widely exploited in the bio-functionalization of SU-8 based microcomponents for advanced Bio-MEMS device applications[2]. A further development in the performance and applications of this class of sensors can be achieved by coupling the outstanding structural properties of SU-8 with the functionalities of colloidal nanocrystals (NCs). Colloidal nano-objects possess a surface organic layer which allows for their positioning on the SU-8 reactive surface conveying to the polymer the unique size and shape tunable functionalities of the nano-entities. This functionalization can contribute to a possible improvement in the sensor sensitivity and specificity. In this work,

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micro mechanical cantilever chips on SU-8 have been functionalized in the dark and at room temperature with oleic acid (OLEA)-capped TiO_2 NCs and Fe_2O_3 NCs before their release from silicon wafer. Such a specific class of NCs was selected for an excellent chemical stability and interesting catalytic, bio/sensing and magnetic properties[3]. The reactivity of the SU-8 surface and that of the OLEA molecules allows for a spontaneous occurrence of an uniform 3D porous network of NCs immobilized on the cantilever surface. Scanning Electron and Atomic Force Microscopy (SEM, AFM) investigations and X-Ray Photoelectron Spectroscopy (XPS) microanalyses have demonstrated that the NCs can firmly bound to the underlying SU-8 with not modifying their morphology and composition, still allowing for an effective chip release and accomplishment of the lithographic fabrication process. The achieved convenient, rapid and robust procedure of functionalization can envision original venues for recognition processes, turning convenient in terms of versatility, specificity and sensitivity of the resulting sensing device.

2. Experimental

Oleic acid (OLEA)-capped Fe_2O_3 NCs have been prepared with a particle size of approximately 11 nm, as reported elsewhere[4]. Rod-shaped TiO_2 NCs have been synthesized as described in [5] with a length of 30 nm and a diameter of 3-4 nm. A surface ligand exchange procedure has been applied to the as synthesized NCs to replace the pristine OLEA coating that may suffer from structural alterations[6] with a fresh one.

The immobilization of the NCs on SU-8 based microcantilevers has been integrated into an existing fabrication method of such microcomponents[7]. The microcantilevers have been soaked in hexane solutions of $1.5*10^{-4}$ M Fe_2O_3 NCs and of 0.05 M TiO_2 NCs, respectively and then washed with pure hexane to remove the NCs not chemically attached. After the functionalization the microcantilevers have been mechanically released from the silicon wafer by means of tweezers. All the fabrication procedures have been performed in a clean room environment.

Topographic AFM images have been collected on UV-exposed SU-8 based patterns. The analyses have been carried out in tapping mode by using a PSIA XE-100 SPM System operating in air and the micrographs have been acquired by sampling the surface with a high frequency silicon cantilever for non-contact/tapping mode (NanoWorld).

SEM investigations have been carried out with a FEI Nova 600 NanoSEM. The imaging has been performed in a low-vacuum-mode where a pressure of 0.6 mbar has been used to minimize charging effects.

X-ray Photoelectron Spectroscopy (XPS) measurements have been performed with a Theta Probe Thermo VG Scientific instrument (base pressure 1×10^{-9} mbar) equipped with a monochromatic AlKα radiation (hν: 1486.6 eV) operating at 300 W. The analyses have been carried out at the 52° Take-off angle (T.O.A.) by means of a 400 μm wide X-ray spot. Samples have been neutralized by means of a flood gun (Mod. 822-06 FG) operating at 400 μA, 40 V and 2×10^{-7} mbar to correct differential or non-uniform charging. The high resolution spectra have been shifted by taking as reference the C_{1s} spectrum centered at 285.0 eV[8].

3. Results and Discussion

A morphological investigation of UV-exposed SU-8 based patterns has been carried out before and after the immobilization of the TiO_2 and Fe_2O_3 NCs. Bare SU-8 based patterns presents a slight rough surface with corrugations high up to 8 nm and a root mean square (RMS) roughness value less than 1 nm (data not reported). Fig. 1 shows the AFM topography images of the patterns modified with the NCs. The figure shows that the NC modified SU-8 presents a highly interconnected layout of irregular and round-shape features that reach maximum heights of 30 nm and 60 nm for the TiO_2 (Fig. 1 a) and Fe_2O_3 NCs (Fig. 1 b), respectively. The RMS values have been estimated at about 2.8 ± 0.2 nm and 4.2 ± 0.2 nm, respectively. Since the heights of such grain-type structures exceed the NC size estimated by TEM investigations[4-5] such a topography can be reasonably accounted for by a random and close packed multilayer network of NCs and/or for by pinholes caused by solvent evaporation[9].

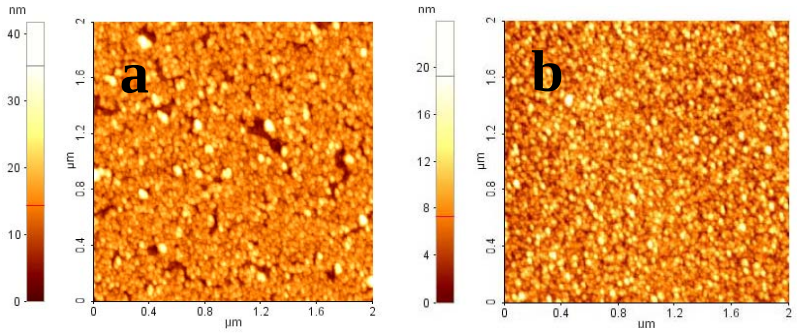

Fig. 1. 2D view of AFM investigation of the TiO_2 (a) and Fe_2O_3 NC (b) modified UV-exposed SU-8 based patterns.

It is worthwhile to notice that investigation has been carried out on bare UV-exposed SU-8 based patterns, as reference sample, soaked in pure hexane has demonstrated a different morphology, showing only the occurrence of swelling of SU-8.

SEM investigations performed on bare and NC modified SU-8 based microcantilevers evidence on large scale a significant modification of the polymer surface morphology upon the immobilization of the NCs (data not shown). Namely, the bare SU-8 based microcantilevers appear relatively smooth and flat, while after their soaking into the NC solution they appear rough and characterized by a quite homogeneous 3D porous coating (data not shown).

In Fig.2 is reported a typical SEM image of released NC functionalized micro cantilever chips. The image evidences that the extensive functionalizion of the SU-8 surface with the NCs does not affect the releasing ability of the chips from the substrate, thus allowing for an effective accomplishment of the lithography fabrication process.

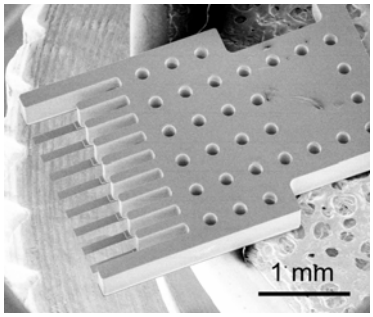

Fig.2. SEM image of a micro mechanical cantilever sensor on TiO_2 NC modified SU-8.

XPS analyses have been performed in order to investigate the nature of the NC attachment on SU-8 and give insight on the possible mechanism. Low resolution XPS spectra and quantitative analyses have shown a change of the SU-8 surface chemistry upon the NC immobilization as shown in Table 1.

Table 1. XPS analysis of the elemental composition of the native and of TiO_2 NC and Fe_2O_3 NC modified cantilever sensor performed at the 52° take-off angle.

sample	%C	%O	%Ti	%Fe
SU8	81.0±0.1	19.0±0.1	--	--
Fe2O3 SU8	67.5±0.4	28.4±0.3	--	4.1±0.5
TiO2 SU8	62.8±0.8	29.9±0.3	7.2±0.5	--

High resolved XPS spectra confirm the chemisorption of Ti^{4+} and Fe^{3+} ions in form of oxides[8] and demonstrate the attachment of the NCs (data not shown).

4. Conclusions

A simple and direct solution-based protocol has been defined to immobilize functional colloidal TiO_2 and Fe_2O_3 NCs on SU-8 based microcantilevers at room temperature and in the dark. The NCs bound the photoresist retaining size, chemical composition and pristine organic surrounding. An extensive surface functionalization of the microcantilevers has been demonstrated by performing AFM, SEM and XPS investigations. In addition, the dense NC coating does not affect the realise properties of the chips allowing an effective accomplishment of the lithography fabrication process. The next step can be now to test the sensing performances of the cantilevers to verify the role played by the morphology and composition effects of the original nanostructured cantilever coating on the selectivity and sensitivity of the sensor. The immobilization procedure can be conveniently extended to colloidal NCs with different composition, size and shape for functionalizing a variety of SU-8 based structural components having different design which can be integrated in Bio-MEMS devices for advanced sensing, environmental and biomedical applications.

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